EXHIBIT D

WATER SOLUBLE ORGANICS
BY DIRECT AQUEOUS INJECTION GAS CHROMATOGRAPHY
WITH FLAME IONIZATION DETECTION

WATER SOLUBLE ORGANICS BY GAS CHROMATOGRAPHY
AND FLAME IONIZATION DETECTION

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1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of various nonhalogenated water soluble volatile organic compounds by direct injection GC/FID. The following compounds can be adequately determined by this method:

Compound Name	Chemical Abstracts No.
2-Methoxyethanol (Methyl Cellosolve)	109-86-4
Diethyl ether	60-29-7
Methanol	67-56-1
Ethanol	64-17-5
n-Propanol	71-23-8
Ethylene Glycol	107-21-1
Propylene Glycol (1,2-Propanediol)	57-55-6
1,4-Dioxane	123-91-1
Dimethyl sulfoxide	67-68-5

1.1.2 As indicated on the chain of custody accompanying each sample delivery group (SDG), the target compound list may be designated as all compounds listed in Exhibit C WSO-FID TCL or a subset of those compounds.

1.2 This method is based on EPA method 8015A. Refer to Exhibit C (WSO-NPD) for a list of the Contract Required Quantitation Limits (CRQLs) for each compound.

1.3 All compound identifications must be supported by an additional qualitative technique. This method also describes the analytical conditions for a second gas chromatographic column that must be used to confirm positive measurements made with the primary column. Confirmed positive results of sufficient concentration must be verified on a GC/MS system.

2.0 SUMMARY OF METHOD

2.1 Water

A 5 ml aliquot of a water sample is transferred to a 10 ml vial and spiked with 10 µl of surrogate spiking solution. A portion of the sample is then transferred to a 2 ml GC vial and 0.5 - 1 µl is injected directly into a gas chromatograph for analysis. The GC is temperature-programmed to separate the organic compounds on a capillary column. Detection is achieved by a flame ionization detector (FID).

2.2 Soil/Sediment/Solid

A 1-2 gram sample of soil, sediment or solid is weighed into a 40 ml VOA vial and spiked with 100 µl of surrogate spiking solution. The vial is filled with reagent water to contain no headspace and extracted in an ultrasonic water bath for 30 minutes. A portion of the sample is then transferred to a 2 ml GC vial and 0.5 - 1 µl is injected directly into a gas chromatograph for analysis. The GC is temperature-programmed to separate the organic compounds on a capillary column. Detection is achieved by a flame ionization detector (FID).

2.3 Method Detection Limits

Prior to analysis, method detection limits (MDLs) for all compounds listed in Exhibit C, Water Soluble Organics - FID, must be established in accordance with Title 40 Code of Federal Regulations, Part 136, Appendix B. The MDL study must be reported as described in Exhibit B. All MDL values determined must be less than or equal to one-third of the CRQL. The MDL study must be conducted using the same specifications as for sample analysis. These specifications include but are not limited to: initial calibration, calibration verification, and continuing calibration technical acceptance criteria, method blank technical acceptance criteria and all instrument operating conditions. The MDL study must be conducted prior to sample analysis, for each alternate column/technique and/or at least annually, whichever, is more frequent. For aqueous samples, seven aliquots of reagent water spiked with each target compound at a concentration of 3 to 5 times the expected MDL are analyzed by direct injection GC/FID. For solid matrices, seven aliquots of a clean solid matrix (such as sand) spiked with each target compound at a concentration of 3 to 5 times the expected MDL are processed through the entire extraction procedure and analyzed by direct injection GC/FID. A 0.5 - 1 µl injection volume is recommended for analysis, however, the same injection volume must be used for all calibration standards, QC samples, sample analyses and MDL studies. All sequential analyses of MDL standards must be reported and used in the resulting MDL values which are calculated. The MDL results are calculated as described in 40 CFR, Part 136, Appendix B and reported as a separate SDG in accordance with Exhibit B. The appropriate Students' t value must be clearly provided with the algorithm used to calculate the MDL values. MDLs shall be determined and reported for each instrument/column and method.

The MDL study must be reported as detailed in Exhibit B. The individual analytical sequence raw data must be provided and these data must be summarized in a table which demonstrates the calculated MDL values. The summarized MDL results table must include the concentration found for each compound in each aliquot, the mean concentration of each compound, the percent recovery of each compound, the standard deviation for each compound, and the Method Detection Limit. The true concentration of the compound in the spike solution must also be provided. The table must list the compounds in the same order as they appear in the target compound list in Exhibit C. In addition, the MDL values for each instrument and method used in reporting results for an SDG shall be submitted with each data package.

The annually determined MDL for an instrument and method shall always be used as the MDL for that instrument/method during that year. If the instrument/method is adjusted in any way that may affect the MDL, the MDL for that instrument/method must be redetermined and the results submitted for use as the established MDL for that instrument/method for the remainder of the year.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

4.1 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A storage blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling will serve as a check on such contamination.

4.2 The laboratory where volatile analysis is performed must be completely free of solvents.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in the chemical analysis.

5.2 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 1,4-Dioxane. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this SOW is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the SDG Narrative.

6.1 Gas chromatograph System

6.1.1 Gas Chromatograph - the gas chromatograph (GC) system must adequately regulate the oven temperature in order to give a reproducible temperature program and must be able to effectively regulate carrier gas flow throughout the analytical run. The system must be suitable for splitless injections and have all required accessories, including detectors, column supplies, gases, and syringes. The carrier gas for routine GC applications is helium. High purity gases must be used to ensure a contaminant free GC system. All gas lines leading to the GC must be constructed from stainless steel or copper tubing and must be solvent rinsed prior to use to eliminate any possible source of contamination. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with rubber components are not to be used.

6.1.2 GC Columns

6.1.2.1 Capillary GC Columns - The following columns are recommended for this analysis. Column length must be a minimum of 30 m, longer lengths may be used. A film thickness of at least 1 µm is recommended because of its larger capacity. A description of the primary and confirmation GC columns used for analysis must be included in the SDG Narrative.

6.1.2.1.1 Primary Column - 30 m x 0.53 mm, bonded; Carbowax 20 M poly (ethylene glycol) with 1.0 µm film thickness, (Supelcowax 10, J&W Scientific DB Wax or equivalent).

6.1.2.1.2 Confirmation Column - 30 m x 0.53 mm, poly (dimethylsiloxane), 5.0 µm film thickness, (Supelco SPB-1, J&W Scientific DB-1, or equivalent).

6.1.2.2 The Contractor may choose to use an alternate capillary column. However, the alternate capillary column selected must meet all the method technical acceptance criteria established in the SOW and Exhibit E.

- The GC column must not introduce contaminants which interfere with identification and quantitation of the compounds listed in Exhibit C (Water Soluble Organics - NPD).
- The GC column must be able to accept concentrations up to the high point standard of each target compound without becoming overloaded.
- The GC column must provide equal or better resolution of the target compounds than the columns listed above.
- The alternate GC column must be used for the entire analysis, including the MDL study, initial and continuing calibration, and all blank, QC sample and all sample analyses. If a new alternate GC column is chosen after the initial MDL study has been completed, then the MDL study must be reanalyzed using that alternate column. The acceptance criteria established in the SOW and Exhibit E must be achieved for these parameters.

6.1.2.2.1 The alternate GC column must be designed to optimize performance. Follow manufacturer's instructions for the use of its product. Before use of any column, other than the ones specified in 6.6.2.2, the Contractor must meet the criteria listed in 6.6.2.2. Once this has been demonstrated, the Contractor must document the column used (brand name, length, diameter, and film thickness) in each SDG Narrative.

6.1.2.2.2 Manufacturer provided technical information concerning the performance characteristics of the GC column must be included in the MDL Study data package to support the use of the alternate column.

6.1.2.2.3 Although the instructions included in the SOW are for wide bore capillary columns, narrower bore capillary columns may be utilized if the criteria in Section 6.6.2.2 are achieved.

6.1.3 Detector - Flame ionization (FID).

6.1.4 Data System - a data system must be interfaced to the GC/NPD. The data system must allow the continuous acquisition of data throughout the duration of the chromatographic program and must permit, at the minimum, the output of time vs. intensity (peak area) data. Also, the data system must be able to rescale chromatographic data in order to report chromatograms meeting the requirements listed within this method. The data system must be capable of flagging all data files that have been edited manually by laboratory personnel since every manual edit must be flagged on the quantitation reports.

6.2 Glassware

6.2.1 Syringes - 5 ml, gas-tight with shut-off valve. Syringe Valve: two-way, with Luer ends (three each).

6.2.2 Microsyringes - 10 µl, 25 µl and 100 µl, 0.006 in. ID needle.

6.2.3 Pasteur Pipets - disposable.

6.2.4 Vials and Caps - 2 ml for GC.

6.2.5 Volumetric Flasks.

6.2.6 Class "A" Volumetric Pipets - 1 ml and 5 ml

6.2.7 Bottle - 10 ml, screw-cap, with Teflon-lined septum.

6.2.8 Bottle - 40 ml, Teflon-lined septum and open top screw cap.

6.3 Balances - analytical, capable of accurately weighing ± 0.0001 g, and a top-loading balance capable of weighing 100 g ± 0.01 g. The balances must be calibrated in accordance with ASTM E 617 specifications each 12-hour work shift. The balances must also be annually checked by a certified technician.

6.4 Porcelain crucibles or aluminum weighing pans

6.5 Drying oven

6.6 Dessicator

6.7 Ultrasonic water bath

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent water - defined as water in which an interferant is not observed at or above the CRQL of the analytes of interest. Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g (1 lb) of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

7.1.1.1 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

7.1.1.2 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90 °C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

7.1.2 Isopropanol - suitable for high resolution gas chromatography

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure described in Exhibit E. The Contractor must be able to verify that the standards are certified by producing the manufacturer's certificates and/or generating the documentation as described in Exhibit E. Manufacturer's certificates of analysis must be retained by the Contractor for the term of the contract and submitted at the completion of the contract performance. The documentation may be requested during an on-site audit.

7.2.2 Stock Standard Solutions

7.2.2.1 Stock standard solutions may be purchased as certified solutions or may be prepared from pure reference materials.

7.2.2.2 Prepare stock standard solutions by placing about 9.8 ml of isopropanol into a 10 ml ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered for about 10 minutes, or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.2.2.3 Using a 100 µl syringe or a pasteur pipet, immediately add about 100 mg (several drops) of assayed reference material to the flask, restopper, then immediately reweigh. The liquid must fall directly into the water without contacting the neck of the flask.

7.2.2.4 Dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in milligrams per milliliter (mg/ml) from the net gain in weight.

7.2.2.5 When compound purity is assayed to be 97.0 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard. If the compound purity is assayed to be less than 97.0 percent, the weight must be corrected when calculating the concentration of the stock solution. See Exhibit E (Analytical Standards Requirements).

7.2.2.6 Transfer the stock solution to a bottle with a teflon-lined screw cap that allows for minimal headspace. Store in the dark at 4 °C (±2 °C). Do not freeze. The concentration of the stock standard solutions, prepared as detailed above, will be approximately 10 mg/ml.

7.2.2.7 Prepare fresh stock standards six months after the date of preparation (or the date opened for purchased stock standards). The stock standards must be replaced sooner if the standard has demonstrated signs of degradation or evaporation.

7.2.3 Secondary Dilution Standards

7.2.3.1 Using stock standard solutions, prepare secondary dilution standards in isopropanol that contain the compounds of interest, either singly or mixed together. Secondary dilution standard solutions should be prepared at concentrations that can be easily diluted to prepare working standard solutions.

7.2.3.2 Secondary dilution standards must be replaced six months after the date of preparation (or the date opened for purchased standards). The standards must be replaced sooner if the standard has demonstrated signs of degradation or evaporation.

7.2.4 Working Standards

7.2.4.1 Surrogate Spiking Solution

Prepare a surrogate spiking solution containing 2-Ethoxyethanol in reagent water at a concentration of 2000 µg/ml. Add 50 µl of this spiking solution to 5 ml of calibration standard, required blank, aqueous sample and aqueous QC sample for a final concentration of 20 µg/ml. Add 500 µl of surrogate spiking solution to all soil/sediment/solid samples, QC samples and required blanks as specified in Section 10.1.4 for a final concentration of 25 µg/ml. Prepare fresh spiking solution weekly, or sooner if the solution has degraded or evaporated.

7.2.4.2 Matrix Spiking Solution

Prepare a matrix spiking solution in reagent water containing 2-Methoxyethanol, n-Propanol and Ethylene Glycol at a concentration of 2000 µg/ml. Refer to Section 12.2.3 for preparation of matrix spike/matrix spike duplicate samples. Prepare fresh spiking solution weekly, or sooner if the solution has degraded or evaporated.

In cases where the site history, previous sampling or sample screening indicates the presence of known target compounds, those compounds shall be included in the matrix spiking solution. The compounds may be substituted for the ones already present or may be included as additional compounds. The matrix spiking solution must contain a minimum of three (3) target compounds. The concentration of each compound in the matrix spiking solution shall remain at 2000 µg/ml. Suspected Target compounds shall be indicated on the chain-of-custody for that SDG.

7.2.4.3 Initial and Continuing Calibration Standards

7.2.4.3.1 Prepare three aqueous initial calibration standard solutions containing all of the target compounds and the surrogate compound at 5, 20 and 100 µg/ml levels.

7.2.4.3.1.1 Calibration standards should be prepared in separate volumetric flasks.

7.2.4.3.1.2 Volumetric flask - add an appropriate volume of the secondary dilution calibration standard solution (Section 7.2.3) and 100 µl of surrogate spiking solution (Section 7.2.4.1) to an aliquot of reagent water in separate 5 ml volumetric flasks. Use a microsyringe and inject the aqueous standards into the expanded area of the filled volumetric flask. Bring to volume. Mix by inverting the flask three times only.

7.2.4.3.2 The continuing calibration standard (Section 9.3) is the midpoint standard used in the initial calibration.

7.2.4.4 Initial Calibration Verification Standard

Prepare an aqueous initial calibration verification standard containing all of the target compounds and the surrogate compound, as in Section 7.2.4.3 above, at the midpoint concentration of the calibration curve. <u>The initial calibration verification standard must be prepared from a source other than that used to prepare the initial calibration standards (e.g. second source verification)</u>.

7.2.5 Ampulated Standard Extracts

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained for 2 years from the manufacturer's preparation date, unless the manufacturer recommends a shorter time period. Standard solutions prepared by the Contractor which are immediately ampulated in glass vials may be retained for 2 years from the Contractor's preparation date. Upon breaking the glass seal, the expiration times listed in Sections 7.2.2 through 7.3 will apply. The Contractor is responsible for assuring that the integrity of the standards has not degraded (see Section 7.3.4).

7.3 Storage of Standard Solutions

7.3.1 Store the stock standards in Teflon-sealed screw-cap bottles with minimal headspace at 4 °C (±2 °C), and protect the standards from light. Fresh standards should be prepared every six months or sooner if comparison with check standards indicates a problem.

7.3.2 Store secondary dilution standards in Teflon-sealed screw-cap bottles with minimal headspace at 4 °C (±2 °C), and protect the standards from light. The secondary dilution standards must be checked frequently for signs of degradation or evaporation, especially just prior to preparing the working standards.

7.3.3 Aqueous standards may be stored for up to 1 week, if held in Teflon-sealed screw-cap vials with zero headspace at 4 °C (±2 °C). Protect the standards from light. All other working standards must be stored at 4 °C (±2 °C).

7.3.4 The Contractor is responsible for maintaining the integrity of standard solutions and verifying prior to use. This means that standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in the solution.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Sample Collection and Preservation

8.1.1 Water samples may be collected in glass containers having a total volume of at least 40 ml with a Teflon-lined septum and an open top screw-cap. If amber containers are not available, the samples must be protected from light. Soil/sediment/solid samples may be collected in glass containers or closed end tubes (e.g., brass sleeves, etc.) in sufficient quantity to perform the analysis. Headspace must be avoided. The specific requirements for site sample collection are outlined by the Region.

8.1.2 For samples received in containers other than glass, the Contractor shall contact the RSCC to ascertain the proper procedure for subsampling from the sample container.

8.1.3 For collection of water samples, the container must be filled by the sampler in such a manner that no air bubbles pass through the sample as the container is being filled. The vial must be sealed by the sampler so that no air bubbles are entrapped in it. Two vials are filled and submitted for analysis.

8.1.3.1 If one water sample vial has an air bubble and the other does not, then use the other vial for analysis.

8.1.3.2 If both vials have air bubbles, then analyze the sample vial which has fewer and/or smaller air bubbles.

8.1.3.3 If both vials have air bubbles greater than pea-size, then the Contractor shall contact the RSCC to ascertain whether or not the sample should be analyzed.

8.1.3.4 For all samples that contain air bubbles, regardless of size, the Contractor shall note the problem, the EPA sample number for the affected samples and any instructions given by the Region in the SDG Narrative.

8.1.4 All samples must be iced or refrigerated at 4 °C (±2 °C) from the time of collection until analysis.

8.2 Procedure for Sample and Sample Extract Storage

8.2.1 The samples must be protected from light and refrigerated at 4 °C (±2 °C) from the time of receipt until 60 days after delivery of a reconciled, complete sample data package to the Agency. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 If sample storage temperatures exceed 4°C (±2 °C) and/or samples are not light protected, then the Contractor shall contact the RSCC to ascertain whether or not the samples should be analyzed. For all samples that were not properly refrigerated and/or light protected, the Contractor shall note the problem, the EPA sample numbers for the affected samples, and the Region's instructions in the SDG Narrative.

8.2.3 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants and in a refrigerator used only for storage of volatile samples.

8.2.4 All volatile samples in an SDG must be stored together in the same refrigerator.

8.2.5 Storage blanks shall be stored with the samples contained in an SDG until all samples are analyzed. The storage blank shall be analyzed concurrently with the last sample in the SDG and the results shall be included in the data package per the reporting requirements contained in Exhibit B.

8.2.6 Samples, sample extracts and standards must be stored separately.

8.2.7 Volatile standards must be stored separately from semivolatile, pesticide/Aroclor and herbicide standards.

8.3 Contract Required Holding Times

8.3.1 Analysis of water and soil/sediment/solid samples must be completed within seven (7) days of Validated Time of Sample Receipt (VTSR). As part of the Agency's QA program, the Agency may provide Performance Evaluation samples which the Contractor is required to prepare per the instructions provided by the Agency. The PE samples must be analyzed and reported with the SDG with which they were submitted.

8.3.2 If volatile samples have exceeded holding times and have not yet been analyzed, then the Contractor shall contact the RSCC to ascertain whether or not the samples should be analyzed. Note that this notification requirement in no way obviates the contractual requirement for the Contractor to analyze samples within holding times. For all samples that exceeded holding times, the Contractor shall note the problem, the EPA sample numbers for the affected samples, and the Region's instructions in the SDG narrative.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Conditions

9.1.1 Gas Chromatograph: The following are the gas chromatographic analytical conditions for the suggested columns. The conditions are recommended unless otherwise noted.

9.1.1.1 Packed columns must not be used for this methodology

9.1.1.2 Capillary Columns:

Temperature program:	45°C (5 min) to 200°C, at 8°C/min; hold for 5 minutes.
Helium carrier flow:	30 - 45 cm/sec
Injection volume:	0.5 - 1 µl
Injector temperature:	250°C
Detector temperature:	300°C

9.1.3 Optimize GC conditions for analyte separation and sensitivity. Water is a difficult solvent to work with on a gas chromatograph, thus the instrument parameters above may require adjustment to optimize the GC to obtain symmetrical peak shape. Once optimized, the same GC conditions must be used for the analysis of all MDL studies, standards, samples, QC samples and required blank analyses. The FID detector settings and gas flows should be set to the manufacturers specifications to achieve optimum performance. Care must be taken to maintain stable and appropriate gas flows to the detector.

9.1.4 The expansion volume of 1 µl of water in an injector at 250 °C, at atmospheric pressure, during a splitless injection is approximately 1.5 ml volume. Thus, in order to reduce injector contamination, the liquid injection volume chosen should meet the specifications of the GC injector system. Autosamplers are the preferred method of injection and may use 0.5 - 1 µl volumes. Manual injections must be 1 µl. The same injection volume must be used for all MDL studies, standards, samples, QC samples and required blanks. The injection volume used must be noted in the SDG Narrative.

9.2 Initial Calibration

9.2.1 Summary of Initial Calibration

9.2.1.1 Prior to the analysis of samples and required blanks, each GC/FID system must be calibrated at a minimum of three concentrations (Section 7.2.4.3) to determine instrument sensitivity and the linearity of the detector response for the target and surrogate compounds.

9.3.1.2 If the technical acceptance criteria for initial calibration are not met, then the Contractor must stop and correct the problem before continuing the analytical sequence.

9.2.2 Frequency of Initial Calibration

9.2.2.1 Each GC/FID system must be initially calibrated upon award of the contract and daily prior to sample analysis, or whenever the Contractor takes corrective action which may change or affect the initial calibration criteria (e.g., column replacement or repair, detector or detector jet cleaning, etc.) or if the continuing calibration technical acceptance criteria have not been met.

9.2.3 Procedure for Initial Calibration

9.2.3.1 Set up the GC/FID system as described in Section 9.1.

9.2.3.2 Prepare the initial calibration standards at the concentrations specified in Section 7.2.4.3.

9.2.3.3 All standards, samples, sample extracts, QC samples, and required blanks must be allowed to warm to ambient temperature before analysis.

9.2.3.4 Analyze the initial calibration sequence as given below.

Injection #	Initial Calibration Standard
1	5 µg/ml Calibration Standard
2	20 µg/ml Calibration Standard
3	100 µg/ml Calibration Standard
4	Instrument Blank
5	Initial Calibration Verification Standard

9.2.4 Calculations for Initial Calibration

9.2.4.1 During the initial calibration, absolute retention times (RT) are determined for all target compounds and the surrogate compound.

9.2.4.2 The RT is measured for each peak (including the surrogate compound) in the three calibration standards and the mean RT is calculated as the average of the three values. Calculate a mean absolute retention time ($\overline{RT}$) for each target compound and the surrogate compound using Equation 1.

EQ. 1

$$\overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n}$$

Where,

$\overline{RT}$ = Mean absolute retention time of analyte.
RT_i = Absolute retention time of analyte.
n = Number of measurements (3).

9.2.4.3 The retention time window (RTW) for each target compound and the surrogate compound is established as ± 0.07 minutes of the mean absolute retention time determined in Section 9.2.4.2. Retention time windows must not overlap, thus close eluting peaks may require a reduced retention time window.

9.2.4.3.1 Alternatively, the RTWs may be established from the most recent MDL study. Determine the absolute retention times of each compound in each of the seven replicates analyzed in determining the aqueous MDLs. Calculate the standard deviation of the retention times of each compound. The retention time window shall be defined as plus or minus three times the standard deviation of the retention times of each target and surrogate compound. Again, retention time windows must not overlap, thus close eluting peaks may require a reduced retention time window.

9.2.4.4 Calculate the calibration factor (CF) for each target and surrogate compound over the initial calibration range using Equation 1.

EQ. 2

$$CF = \frac{A_x}{C_x}$$

Where,

A_x = Peak Area of the compound to be measured,

C_x = Concentration of the compound to be measured (mg/L)

9.2.4.5 The linearity of the instrument is determined by calculating the percent relative standard deviation (%RSD) of the calibration factors from the three-point initial calibration curve. Using equations 3 and 4, calculate the mean calibration factor and the percent relative standard deviation for each target compound and the surrogate compound.

EQ. 3

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

EQ. 4

$$\%RSD = \frac{SD_{CF}}{\overline{CF}} \times 100$$

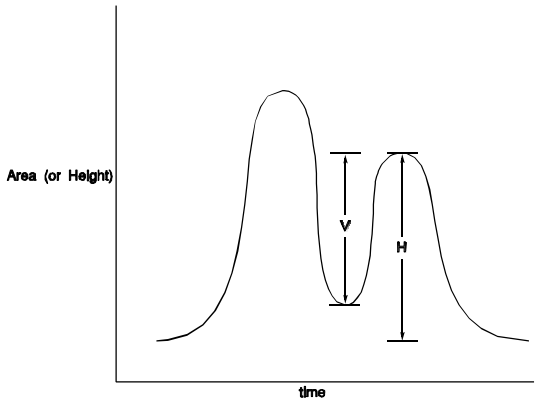
Where,

$$SD_{CF} = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{(n-1)}}$$

%RSD = Percent relative standard deviation
SD_{CF} = Standard deviation of calibration factors
CF_i = Calibration factor

$\overline{CF}$ = Mean calibration factor
n = Total number of values (3)

9.2.4.6 Calculate the resolution between each target compound and surrogate in the mid point standard of the initial calibration using Equation 5.



EQ. 5

$$\%Resolution = \frac{V}{H} \times 100$$

Where,

V = Depth of the valley between the two peaks. The depth of the valley is measured along a vertical line from the level of the apex of the shorter peak to the floor of the valley between the two peaks.

H = Height of the shorter of the adjacent peaks.

9.2.4.4 Calculate the concentration for each target compound in the initial calibration verification standard using equation 4. Calculate the percent difference (% D) between the amount of each compound (including the surrogates) found in the verification standard and the nominal amount using equation 5.

EQ. 6

$$C_{calc} = Amount\ found\ (mg/L) = \frac{Peak\ Area\ of\ compound}{\overline{CF}}$$

Where,

$\overline{CF}$ = The mean calibration factor of the compound determined in the most recent initial calibration.

EQ. 7

$$\%\ Difference = \frac{C_{calc} - C_{nom}}{C_{nom}} \times 100$$

Where,

C_{nom} = Nominal concentration of each compound.

C_{calc} = Calculated concentration of each compound using the initial calibration.

9.2.5 Technical Acceptance Criteria for Initial Calibration

All initial calibration technical acceptance criteria apply independently to both GC columns.

9.2.5.1 The initial calibration sequence must be analyzed according to the procedure and in the order listed in Section 9.2.3.4, at the concentration levels described in Section 7.2.4.3 and at the frequency listed in Section 9.2.2.

9.2.5.2 The absolute retention time of each target and surrogate compound must be within the established RTWs (Section 9.2.4.3).

9.2.5.3 The %RSD of the calibration factors for each target component must be less than or equal to 20 percent (≤ 20%). The %RSD of the calibrations factor for the surrogate must be less than or equal to 30 percent. One target compound per column may exceed the 20 percent limit for %RSD but that compound must have a %RSD of less than or equal to 25 percent.

9.2.5.4 The resolution between two adjacent peaks in the mid point initial calibration standard must be greater than or equal to 60.0 percent.

9.2.5.5 The percent difference of the calculated amount (amount found) and the nominal amount (amount added) for each target and surrogate compound in the initial calibration verification standard of each GC column must be greater than or equal to -25.0 AND less than or equal to 25.0 percent.

9.2.5.6 All instrument blanks must meet the technical acceptance criteria specified in Section 12.1.3.4.

9.2.5.7 The identification of target compounds by gas chromatographic methods is based primarily on retention time data. The retention time of the apex of a peak can only be verified from an on-scale chromatogram. Therefore, the following requirements apply to all data presented.

- The chromatograms that result from the analyses of the initial calibration sequence must display the analytes present in each standard at greater than 10 percent of full scale but less than 100 percent of full scale.
- The chromatograms for at least one of the three analyses from the initial calibration sequence must display the analytes at greater than 50 percent and less than 100 percent of full scale.
- If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.
- If the chromatogram of any standard needs to be replotted electronically to meet these requirements, both the initial

chromatogram and the replotted chromatogram must be submitted in the data package.

9.2.6 Corrective Action for Initial Calibration

9.2.6.1 If any technical acceptance criteria for the initial calibration are not met, inspect the system for problems. It may be necessary to change the column, clean the detector or detector jet, clean the injection port, or take other corrective actions to achieve the acceptance criteria.

9.2.6.2 Initial calibration technical acceptance criteria **must** be met before any samples, QC samples or required blanks are analyzed. Any samples, QC samples or required blanks analyzed before the initial calibration technical acceptance criteria have been met shall require reanalysis at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample technical acceptance criteria.

9.2.6.3 Sample analyses reported with a non-compliant initial calibration after reanalysis shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability.

9.3 Continuing Calibration

9.3.1 Summary of Continuing Calibration

Two types of analyses are used to verify the calibration and evaluate instrument performance. The analysis of an instrument blank and the continuing calibration standard (Section 7.2.4.3.3) constitute the continuing calibration. Sample data are not acceptable unless bracketed by acceptable analyses of instrument blanks and continuing calibration standards.

9.3.2 Frequency of Continuing Calibration

The initial calibration must be verified every 12 hours and after the last sample in the SDG with the analysis of an instrument blank and continuing calibration standard. **These time requirements for verifying the initial calibration are a minimum and more frequent analyses may be advantageous to monitor the calibration so that the analytical sequence may continue**.

9.3.2.1 For the 12-hour period immediately following the initial calibration sequence, the instrument blank and initial calibration verification standard that are the last two steps in the initial calibration sequence bracket the front end of the first 12-hour period. The injection of the instrument blank immediately following the initial calibration standards starts the beginning of the first 12-hour period. Samples may be injected for 12-hours from the injection of the instrument blank. The two injections immediately after that 12-hour period must be an instrument blank and a continuing calibration standard. The instrument blank must be analyzed first.

9.3.2.2 The analysis of the instrument blank and the continuing calibration standard immediately following the first 12-hour period may be used to begin the next 12-hour period to complete the analysis of the remaining samples in the SDG, provided that they meet the acceptance criteria in Section 9.3.5. This next 12-hour period must be bracketed by the acceptable analysis of an instrument blank and a continuing calibration standard, in that order. If more than 24 hours is required to complete the remaining samples in an SDG from an "on-going" analysis sequence, the last instrument blank and continuing calibration standard may in turn be used to bracket the front end of yet another 12-hour period to complete the analysis.

9.3.2.3 If the entire 12-hour period is not required for the analyses of all samples in the SDG, the sequence must be ended with the instrument blank/continuing calibration standard combination.

9.3.3 Procedure for Continuing Calibration

9.3.3.1 Analyze the instrument blank and continuing calibration standard at the required frequencies (Section 9.3.2). The concentration of the continuing calibration standard is that of the midpoint standard of the initial calibration and should be prepared from the same standard solution.

9.3.3.2 All standards and blanks must be at ambient temperature at the time of preparation and analysis.

9.3.4 Calculations for Continuing Calibration

9.3.4.1 Calculate the concentration for each target and surrogate compound in the continuing calibration standard using equation 6. Calculate the percent difference (% D) between the amount of each target and surrogate compound found in the continuing calibration standard and the nominal amount using equation 7.

9.3.5 Technical Acceptance Criteria for Continuing Calibration

All continuing calibration technical acceptance criteria apply independently to each column. Each column must meet criteria.

9.3.5.1 The continuing calibration standards and instrument blanks must be analyzed at the required frequency, as specified in Section 9.3.2, on a GC/FID system that has met the initial calibration technical acceptance criteria.

9.3.5.2 The absolute retention time of each target and surrogate compound in the continuing calibration standard must be within the RT windows established in Section 9.2.4.3.

9.3.5.3 The percent Difference (%D) between the calculated amount (amount found) and the nominal amount (amount added) for each target and surrogate compound must be less than or equal to 25 percent and greater than or equal to -25 percent ($-25\% \geq \%D \leq 25\%$).

9.3.5.4 All instrument blanks must meet the technical acceptance criteria in Section 12.1.3.4.

9.3.5.5 Target compound identification by gas chromatographic methods is based primarily on retention time data. The retention time of the apex of a peak can only be verified from an on-scale chromatogram. Therefore, the following requirements apply to all data presented.

- The chromatograms that result from the analyses of the continuing calibration standard and instrument blank must display the analytes present at greater than 10 percent and less than 100 percent of full scale.
- If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.
- If the chromatogram of any standard needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

9.3.6 Corrective Action for Continuing Calibration

9.3.6.1 If the technical acceptance criteria for the instrument blank and continuing calibration standard are not met, inspect the system for problems and take corrective action to achieve the acceptance criteria.

9.3.6.2 Major corrective actions such as replacing the GC column or cleaning the detector or detector jet shall require that a new initial calibration be performed that meets the technical acceptance criteria in Section 9.2.5.

9.3.6.3 Minor corrective actions may not require performing a new initial calibration, provided that the reanalysis of the instrument blank

and continuing calibration standard (that originally failed the criteria) now meet all of the continuing calibration technical acceptance criteria. Any samples, QC samples and required blanks that were analyzed between the last compliant continuing calibration standard and the continuing calibration standard that required minor corrective action shall require reanalysis at no additional cost to the Agency.

9.3.6.4 If a continuing calibration standard does not meet technical acceptance criteria listed in Section 9.3.5, it must be reinjected immediately. If the second injection of the continuing calibration standard meets the criteria, sample analysis may continue. If the second injection does not meet the criteria, all data collection must be stopped. Appropriate corrective action must be taken, and a new initial calibration sequence must be analyzed before more sample data are collected.

9.3.6.5 If an instrument blank does not meet the technical acceptance criteria listed in Section 12.1.3.4, all data collection must be stopped. Appropriate corrective action must be taken to provide a contaminant free system, and an acceptable instrument blank must be analyzed before more sample data are collected.

9.3.6.6 Analysts are reminded that analyzing an instrument blank and a continuing calibration standard once every 12 hours is the minimum contract requirement. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to analyze instrument blanks and continuing calibration standards more often to avoid discarding data.

9.3.6.7 If a successful instrument blank and continuing calibration standard cannot be analyzed after an interruption in analysis, an acceptable initial calibration must be analyzed before sample data may be collected. All acceptable sample analyses must be preceded and followed by compliant instrument blanks and continuing calibration standards, as described in Section 9.3.2.

9.3.6.8 Continuing calibration technical acceptance criteria must be met before any samples, QC samples and required blanks are reported. Any samples, QC samples and required blanks associated with a continuing calibration standard which did not meet the technical acceptance criteria will require reanalysis at no additional cost to the Agency.

9.3.6.9 Sample analyses reported with a non-compliant continuing calibration after reanalysis shall receive a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the non-compliance on data usability

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample weight/volume (less than 90% of the required weight/volume) is received to perform the analyses, the Contractor shall contact the RSCC for instructions. The Region will either require that sample analyses not be performed or will require that a reduced volume be used for the sample analysis. Changes in the sample analysis must be preapproved by the Region. The Contractor shall document the problem, EPA sample numbers for the affected samples, and the Region's instructions (including sample weight/volume prepared and analyzed) in the SDG Narrative.

10.1.2 If multiphase samples (e.g., two-phase liquid sample, oily sludge/sandy soil sample) are received by the Contractor, then the Contractor shall notify the RSCC that a multiphase sample has been received. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do one of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample and analyze each phase separately. The RSCC will provide EPA sample numbers for the additional phases, if required.
- Separate the phases of the sample and analyze one or more of the phases, but not all of the phases. The RSCC will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope of the method), then the Region may require the Contractor to do one of the following:

- Separate the phases and analyze the phase(s) that is amenable to analysis. The RSCC will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the problem, the EPA sample numbers for the affected samples, and the Region's instructions in the SDG Narrative.

10.1.3 Water Samples

10.1.3.1 All water samples must be allowed to warm to ambient temperature before analysis.

10.1.3.2 Pipet a 5 ml aliquot of the aqueous sample to a separate 10 ml vial, add 50 µl surrogate spiking solution (Section 7.2.4.1) and swirl gently to mix. Transfer a portion of the sample to a 2 ml GC vial and proceed immediately to GC/NPD analysis, Section 10.2.

10.1.4 Soil/Sediment/Solid Samples

10.1.4.1 The sample (for water soluble organics) is defined as the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula.

10.1.4.4 Weigh 1.5-2.0 g of sample into a tared 40 ml VOA vial. Using a clean metal spatula, carefully break up any lumps of sample. Record the sample weight to the nearest 0.01 g.

10.1.4.5 Re-tare the 40 ml vial. Add 500 µl of surrogate spiking solution (Section 7.2.4.1), fill the vial with reagent water and cap so there is no headspace.

10.1.4.6 Dry the outside of the vial with an absorbent cloth and re-weigh the vial (to the nearest 0.1 g) to determine the weight of water present. Assuming a density of water equal to 1 g/ml, determine the volume of water present to the nearest milliliter.

10.1.4.6 Place the vial in an ultrasonic water bath for 30 minutes to adequately extract the soil sample. Following sonication, invert the vial 3 times to mix the extract.

10.1.4.7 Let the extracted sample settle and cool to room temperature. Then using a disposable pipet, transfer an aliquot of the aqueous supernatant to a separate GC vial and proceed immediately to GC/NPD Analysis, Section 10.2.

10.1.4.8 Percent Moisture Determination

Immediately after weighing the sample for analysis, weigh 5-10 g of the soil/sediment/solid, to the nearest 0.01 g, into a tared crucible. Determine the percent moisture by drying the sample overnight at 105 °C. Allow the sample to cool in a desiccator prior to weighing. Calculate the percent moisture according to equation 8 below. Concentrations of individual compounds will be reported relative to the dry weight of soil/sediment/solid.

EQ. 8

$$\%moisture = \frac{g\ of\ wet\ sample - g\ of\ dry\ sample}{g\ of\ wet\ sample} \times 100$$

10.2 GC/FID Analysis

10.2.1 Introduction to Sample Analysis by GC/FID

10.2.1.1 Before samples, QC samples or required blanks can be analyzed, the instrument must meet the initial calibration technical acceptance criteria specified in Section 9.2.5.

10.2.1.2 Positive sample results (a peak present on the primary column that is within the retention time window of a target compound and that calculates to a concentration greater than the CRQL) shall require second column confirmation. The confirmatory column must also meet the initial calibration technical acceptance criteria.

10.2.1.3 Standards, samples, QC samples and required blanks must be analyzed within an analytical sequence, as defined in Section 10.2.2.1, under the same instrumental conditions.

10.2.1.4 Set up and optimize the GC/FID system per the requirements in Section 9.0.

10.2.2 Procedure for Sample Analysis by GC/FID

Sample analysis must begin immediately after the headspace of the 40 ml sample vial is broken. For aqueous samples, this means immediately after sample preparation and for soils/sediment/solid samples, this means immediately after the extraction is complete and the vial is opened. Either automatic or manual injection may be used. If autosamplers are used, 0.5 - 1 µl injection volumes may be used. Manual injections must use 1 µl injection volumes. Injection volumes of greater than 1 µl may be used if the injector system is capable of handling the expansion volume (refer to manufacturer for technical assistance if needed). The same injection volume must be used for all MDL studies, standards, samples, QC samples and required blanks. The injection volume used must be noted in the SDG Narrative.

10.2.2.1 Analytical Sequence

All samples must be analyzed within a valid analytical sequence as given below.

Time	Injection #	Material Injected
0 hr.	1 - 3	Initial calibration Standards
	4	Instrument blank
	5	Initial calibration verification standard (second source)
	6	First sample - Method Blank
	7...	Subsequent samples
12 hr.	x	Last sample
0 hr.	1st inj. past 12 hr.	Instrument blank
	2nd inj. past 12 hr.	Continuing calibration standard
	x...	Subsequent samples
≤12 hr.	Last sample in SDG	Last sample
	2nd to last inj.	Instrument blank
	Last injection	Continuing calibrationm standard

10.2.2.1.1 NOTE: The first 12 hours are counted from injection #4 (the instrument blank at the end of the initial calibration sequence), not from injection #1. Samples may be injected until 12 hours have elapsed. The following 12-hour period is timed from the injection of the instrument blank that brackets the front end of the samples. Because the 12-hour time period is timed from injection of the instrument blank until the injection of the last sample, each 12-hour period may be separated by the length of one chromatographic run, that of the analysis of the last sample. While the 12-hour period may not be exceeded, the laboratory may run instrument blanks and continuing calibration standards more frequently if it is to their benefit.

10.2.2.1.2 After an acceptable initial calibration (Section 9.2), the analytical sequence may continue until the last sample in the SDG as long as acceptable instrument blanks and continuing calibration standards are analyzed at the required frequency. This analytical sequence indicates only the minimum required blanks and continuing calibration standards. More blanks and continuing calibration standards may be analyzed at the discretion of the Contractor provided they meet the technical acceptance criteria for continuing calibration, Section 9.3.5.

10.2.2.1.3 An analytical sequence must include all required matrix spike/matrix spike duplicate and blank analyses. The method blank that is prepared/extracted with a particular set of samples shall be analyzed after a compliant initial calibration verification standard and prior to sample analyses. This method blank must also be analyzed with any samples from that set that are analyzed for second column confirmation. The storage blank must be analyzed concurrently with the last

sample in the SDG (refer to 12.1.4). The Contractor may decide at what point in the sequence the matrix spike/matrix spike duplicate are to be analyzed. Matrix spike/matrix spike duplicate samples shall require second column confirmation only if positive results are observed in the original unspiked sample.

10.2.2.1.4 The requirements for the analytical sequence apply to both GC columns and for all instruments used for these analyses.

10.2.3 Sample Dilutions

10.2.3.1 If the concentration of any target compound in any sample or QC sample exceeds the initial calibration range, a fresh aliquot from the prepared or extracted sample must be diluted and reinjected. Guidance in performing dilutions and exceptions to this requirement are given in Sections 10.2.3.2 through 10.2.3.8.

10.2.3.2 Use the results from the original analysis to determine the approximate dilution factor required to get the largest target compound peak within the initial calibration range.

10.2.3.3 The dilution factor chosen should keep the response of the largest target compound peak in the upper half of the initial calibration range of the instrument.

10.2.3.4 All dilutions shall be made in volumetric flasks (10 ml to 100 ml).

10.2.3.5 Select the smallest volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

10.2.3.6 Add an appropriate aliquot of aqueous sample or sample extract into the volumetric flask. Dilute the flask to the mark with reagent water. Cap the flask, invert, and shake three times.

10.2.3.7 If this is an intermediate dilution, repeat the above procedure to achieve further dilutions.

10.2.3.8 Do **not** submit data for more than two analyses, i.e., the original sample analysis and **one** dilution, or, from the most concentrated dilution analyzed and one further dilution. This statement does not refer to reanalyses required due to failed technical acceptance criteria.

10.2.3.9 The Contractor may receive instructions with the sampling paperwork which requires that all samples be analyzed undiluted in addition to the other dilutions required to bring all target compounds within the linear range. This may be required in instances where the CRQLs for all target compounds must be achieved even though one or more target compounds exceed the calibration range and/or high concentrations of non-target compounds are present. For all samples affected by this situation, the Contractor shall note any problems encountered, the EPA sample numbers affected by this situation and the Region's instructions presented with the sample paperwork in the SDG Narrative.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

11.1.1.1 The laboratory shall identify and quantitate analyte peaks based on the RT windows and the mean calibration factor, respectively, established during the initial calibration sequence.

11.1.1.2 All sample results that contain a peak within the retention time window of a target compound on the primary column, that calculates to a concentration greater than or equal to the CRQL, must be confirmed by second column analysis. All technical acceptance criteria established for the primary column analysis must be applied and met for the confirmation analysis.

11.1.1.3 An analyte is identified when a peak is observed in the appropriate RT windows on both GC columns. Sample concentrations must be calculated for both the primary and secondary columns and must be reported on Form X along with the percent difference between the two values. The lower of the two calculated sample concentrations shall be reported on Form I.

11.1.2 GC/MS Confirmation of Target Volatiles

11.1.2.1 Any target compound reported on Form I at a concentration greater than the CRQL must have the identification confirmed by GC/MS analysis if the concentration is sufficient for that purpose. The following paragraphs are to be used as guidance in performing GC/MS confirmation. If the Contractor fails to perform GC/MS confirmation as appropriate, then the Agency may require reanalysis of any affected samples at no additional cost to the Agency.

Sample analyses reported without required GC/MS confirmation may be subject to a commensurate reduction in sample price or zero payment due to data rejection, depending upon the impact of the non-compliance on data usability.

11.1.2.2 In order to confirm the target compound identification of samples analyzed on the GC/MS, the laboratory must also analyze a reference standard of each target compound present. To demonstrate the ability of the GC/MS system to identify the analyte in question, the concentration of the reference standard should be approximately 10 times the GC/MS limit of detection. For direct aqueous injection on the GC/MS, a 25 µg/ml target compound concentration should be sufficient for this purpose.

11.1.2.3 In addition, when performing GC/MS confirmation, the method blank extracted and/or analyzed with that sample set, must also be analyzed by GC/MS to demonstrate that the presence of the analyte was not the result of laboratory contamination.

11.1.2.4 For GC/MS confirmation of target compounds, the required deliverables are copies of the analyte spectrum for the sample, any library search results (best TIC matches), the reference standard spectrum, and the method blank spectrum. Also include the extracted ion current profile (EICP) of the base peak from the sample, reference standard, and method blank analyses.

11.1.2.5 If the identification of the analyte cannot be confirmed by the GC/MS procedures above and the concentration calculated from the GC/FID analysis is greater than or equal to the concentration of the reference standard analyzed by GC/MS, then report the analyte as undetected, adjust the sample quantitation limit (the value associated with the "U" qualifier) to a sample concentration equivalent to the concentration of the GC/MS reference standard, and qualify the results on Form I with one of the laboratory-defined qualifiers ("X," "Y," or "Z"). In this instance, define the qualifier explicitly in the SDG Narrative, and include the EPA sample numbers affected and the steps taken to confirm the analyte.

11.2 Calculations

11.2.1 Target Compounds

The concentrations of the target compounds and surrogate are calculated separately for both GC columns by using the following equations:

11.2.1.1 Water

EQ. 7

$$Concentration\ \mu g/L = \frac{(A_x)(Df)}{(\overline{CF})}$$

Where,

A_x = Area of the peak for the compound to be measured.

$\overline{CF}$ = The mean calibration factor of the compound determined in the most recent initial calibration.
Df = Dilution factor. If no dilution is performed, Df = 1.0.

11.2.1.2 Soil/Sediment/Solid

Note: Soil/Sediment/solid samples shall be reported on a "dry weight" basis.

EQ. 8

$$Concentration\ \mu g/Kg = \frac{(A_x)(V_t)(Df)}{(\overline{CF})(W_s)(D)}$$

Where,

A_x and $\overline{CF}$ are as given for water, above.
V_t = Volume used to extract the soil/sediment/solid sample (40 ml).

$$D = \frac{100 - \%\ moisture}{100}$$

W_s = Weight of sample extracted in grams (1.5 - 2 g)
Df = Dilution factor. If no dilution is performed, Df = 1.0.

11.2.1.2.1 Because of the likelihood that compounds co-eluting with the target compounds will cause positive interferences and increase the concentration determined by the method, the lower of the two concentrations is reported on Form I. In addition, the concentrations calculated for both the GC columns are reported on Form X, along with a percent difference comparing the two concentrations. The percent difference is calculated according to Equation 9.

EQ. 9

$$\%D = \frac{Conc_H - Conc_L}{Conc_L} \times 100$$

Where,

$Conc_H$ = The higher of the two concentrations for the target compound in question

$Conc_L$ = The lower of the two concentrations for the target compound in question

11.2.1.2.2 Note that using this equation will result in percent difference values that are always positive. The value will also be greater than a value calculated using the higher concentration in the denominator; however, given the likelihood of a positive interference raising the concentration determined on one GC column, this is a conservative approach to comparing the two concentrations.

11.2.2 CRQL Calculation

If the adjusted CRQL is less than the CRQL listed in Exhibit C (Water Soluble Organics - FID), report the CRQL in Exhibit C. If the adjusted CRQL is greater than the CRQL listed in Exhibit C (Water Soluble Organics - NPD), report the adjusted CRQL.

11.2.2.1 Water Samples

EQ. 10

$$\underset{CRQL}{Adjusted} = \underset{CRQL}{Contract} \times \frac{(V_x)(Df)}{(V_o)}$$

Where,

V_o = Actual sample volume.
V_x = Contract sample volume (5.0 ml).
Df = Dilution factor (If no dilution performed, Df = 1)

11.2.2.2 Soil/Sediment/Solid Samples

EQ. 11

$$\underset{CRQL}{Adjusted} = \underset{CRQL}{Contract} \times \frac{(W_x)(Df)}{(W_s)(D)}$$

Where,

W_s, Df and D are as given in equation 8.
W_x = Contract sample weight (1.0 g dry weight soil/sed/solid).

11.2.3 Surrogate Recoveries

11.2.3.1 The concentration of the surrogate is calculated separately for each GC column in a similar manner as the other analytes, using Equations 7 and 8. Use the mean calibration factor determined from the initial calibration. The recovery of the surrogate is calculated for each GC column according to Equation 12.

EQ. 12

$$Percent\ Recovery = \frac{Q_d}{Q_a} \times 100$$

Where,

Q_d = Quantity determined by analysis
Q_a = Quantity added

11.2.3.2 The advisory limits for the recovery of the surrogate is 70 - 130 percent.

11.2.3.3 As these limits are only advisory, no further action is required by the laboratory if these limits are not achieved; however, frequent failures to meet the limits for surrogate recovery warrant investigation by the laboratory, and may result in questioning from the Agency.

11.3 Technical Acceptance Criteria for Sample Analysis

The requirements below apply independently to each GC column and to all instruments used for these analyses.

Sample results for target compounds found to be present on the primary column at a concentration above the CRQL must be confirmed by second column analysis. Quantitation must be performed for each GC column (primary and confirmatory) for which samples, QC samples and required blanks were analyzed.

11.3.1 Samples must be analyzed under the GC/FID operating conditions in Section 9.1. The instrument must have met all initial calibration, continuing calibration and blank technical acceptance criteria. Sample data must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, and continuing calibration standards, as described in Section 9.3.

11.3.2 The samples must be extracted and analyzed within the contract required holding times.

11.3.3 The samples must have an associated method blank meeting the technical acceptance criteria for method blanks (Section 12.1.2).

11.3.4 The retention time for the surrogate must be within the retention time window as calculated in Section 9.2.4.2 for both GC columns.

11.3.5 No target analyte concentrations may exceed the upper limit of the initial calibration, or else the sample or extract must be diluted and reanalyzed as described in Section 10.2.3.

11.3.6 The identification of target compounds by gas chromatographic methods is based primarily on retention time data. The retention time of the apex of a peak can be verified only from an on-scale chromatogram. The following requirements apply to all data presented for direct aqueous injection analyses.

11.3.6.1 When no analytes are identified in a sample, the chromatograms from the analyses of the sample must use the same scaling factor as was used for the low point standard of the initial calibration associated with those analyses.

11.3.6.2 Chromatograms must display target compounds detected in the sample at less than full scale.

11.3.6.3 If a sample must be diluted, chromatograms must display target compound peaks between 10 and 100 percent of full scale.

11.3.6.4 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.

11.3.6.5 If the chromatogram of any sample needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

11.3.7 The Contractor must demonstrate that there is no carryover from a contaminated sample before data from subsequent analyses may be submitted. After a sample that contains a target compound at a level exceeding the initial calibration range, the Contractor must either:

- Analyze an instrument blank immediately after the contaminated sample. The instrument blanks must meet the technical acceptance criteria for blank analysis (see Section 12.1.4), or
- Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample and that exceeded the calibration range. The maximum contamination criteria are as follows: the sample must not contain a concentration above the CRQL for the target compounds that exceeded the limits in the contaminated sample. If the maximum criteria were exceeded, then all samples affected by the carryover must be reanalyzed at no additional cost to the Agency.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample analysis technical acceptance criteria MUST be met before data are reported. Samples contaminated from laboratory sources or associated with a contaminated method blank will require re-extraction and reanalysis at no additional cost to the Agency. Any samples analyzed that do not meet the technical acceptance criteria will require re-extraction and/or reanalysis at no additional cost to the Agency.

11.4.2 If the sample analysis technical acceptance criteria are not met, check calculations, surrogate solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the technical acceptance criteria, in which case, the affected samples must be reanalyzed at no additional cost to the Agency after the corrective action.

11.4.3 If sample chromatograms have a high baseline or interfering peaks, inspect the system to determine the cause of the problem (e.g. carryover, column bleed, dirty detector, contaminated gasses, leaking septum, etc.). After correcting the problem, analyze an instrument blank to demonstrate that the system is functioning properly. Reanalyze the affected samples or sample extracts. If the problem with the samples or sample extracts still exists, then those samples must be re-extracted and/or reanalyzed. Samples which cannot be made to meet the given specifications after one re-extraction/reanalysis are reported in the SDG Narrative and do not require further analysis.

11.4.4 Sample analyses reported with non-compliant initial calibration, initial calibration verification, continuing calibration or method/instrument/storage blanks shall be subject to a commensurate reduction in sample price or zero payment due to data rejection, depending upon the impact of the non-compliance on data usability.

12.0 QUALITY CONTROL

12.1 Blank Analyses

12.1.1 Introduction

There are three types of blanks always required by this method: the method blank, the instrument blank and the storage blank. The method, instrument and storage blanks must meet their respective acceptance criteria for the sample analysis acceptance criteria to be met.

12.1.2 Method Blanks

12.1.2.1 Summary of Method Blanks

A method blank is a volume of a clean reference matrix (reagent water for water samples or a purified solid matrix soil/sediment/solid samples) that is prepared and carried through the entire analytical procedure with samples of similar matrix in the SDG. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

12.1.2.2 Frequency of Method Blanks

A method blank must be prepared/extracted once for the following, whichever is most frequent, and analyzed on each GC/FID system and column (primary and secondary) along with those samples which it is associated with:

- Each SDG (not to exceed 20 field samples), or
- Each matrix within an SDG, or
- Each preparation/extraction procedure within an SDG, or
- Whenever samples are prepared/extracted.

12.1.2.3 Procedure for Method Blank Preparation

12.1.2.3.1 For direct aqueous injection of water soluble organics, a method blank for water samples consists of 5 ml of reagent water spiked with 10 µl surrogate spiking solution (Section 7.2.4.1). For soil/sediment/solid samples, the method blank consists of 1.5 - 2.0 g of purified solid matrix weighed into a 40 ml VOA vial. The blank is then spiked with 100 µl surrogate spiking solution and diluted with reagent water and capped so that no headspace is present. The vial is then re-weighed to determine the amount of water present (refer to section 10.1.4).

12.1.2.3.2 Prepare/extract and analyze method blanks along with samples according to Section 10.

12.1.2.3.3 Calculate method blank results according to Section 11.

12.1.2.4 Technical Acceptance Criteria for Method Blanks

12.1.2.4.1 The requirements below apply independently to each GC column and to all instruments used for these analyses.

12.1.2.4.2 All method blanks must be prepared and analyzed at the frequency described in Section 12.1.2.2 using the procedure above and in Section 10 on a GC/FID system meeting the initial calibration and continuing calibration technical acceptance criteria.

12.1.2.4.3 The concentration of the target compounds in the method blank must be less than the CRQL for each target compound.

12.1.2.4.4 The method blank must meet all sample technical acceptance criteria in Section 11.3.4 to 11.3.6.

12.1.2.4.5 Surrogate recoveries must fall within the acceptance windows of 70-130%. In the case of method blank(s), these limits are not advisory.

12.1.2.5 Corrective Action for Method Blanks

12.1.2.5.1 If a method blank does not meet the technical acceptance criteria, the Contractor must consider the system to be out of control.

12.1.2.5.2 If contamination is a problem, then the source of the contamination must be investigated and appropriate corrective action measures must be taken and documented before further sample analysis proceeds. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and sample processing hardware that lead to discrete artifacts and/or elevated baselines be investigated and appropriate corrective actions be taken and documented before further sample analysis. All samples associated with a contaminated method blank must be re-extracted/reanalyzed at no additional cost to the Agency.

12.1.2.5.3 If the surrogate recovery in the method blank does not meet the acceptance criteria listed in 12.1.2.4.5, first reanalyze the method blank. If surrogate recoveries do not meet the acceptance criteria after reanalysis, the method blank and all samples associated with that method blank must be re-prepared/re-extracted and reanalyzed at no additional cost to the Agency.

12.1.2.5.4 If the technical acceptance criteria for method blank analyses are not met, then the contractor must stop and correct the problem before continuing the analytical sequence. If sample analyses are reported with non-compliant method blanks, then the contractor shall receive a commensurate reduction in sample price or zero payment depending upon the impact of the non-compliance on data usability.

12.1.3 Instrument Blanks

12.1.3.1 Summary of Instrument Blanks

An instrument blank is reagent water that contains the surrogate compound at a concentration of 200 µg/L. Instrument blanks are analyzed as part of the initial and continuing calibrations and after a sample or sample dilution which contains a target compound that exceeds the initial calibration range or a non-target compound which interferes with the retention time window of a target compound. Instrument blanks must be analyzed to demonstrate that the GC system is free of contamination.

12.1.3.2 Frequency of Instrument Blanks

The first analysis in a 12-hour analytical sequence must be an instrument blank. All acceptable sample analyses are to be bracketed by acceptable instrument blanks, as described in Section

10.2.2.1. An instrument blank must also be analyzed immediately after a contaminated sample to verify there is no carryover.

12.1.3.3 Procedure for Instrument Blanks

12.1.3.3.1 Prepare the instrument blank by adding 10 µl of the surrogate spiking solution to 5 ml reagent water for a concentration of 200 µg/L of N,N-Dimethylacetamide.

12.1.3.3.2 Analyze the instrument blank according to Section 10 at the frequency listed in Section 12.1.3.2.

12.1.3.3.3 Calculate the concentration of each analyte detected in the instrument blank using equation 7. Compare the results to one-half the CRQL values for target compounds in water samples.

12.1.3.4 Technical Acceptance Criteria for Instrument Blanks

12.1.3.4.1 All instrument blanks must be prepared and analyzed at the frequency described in Section 12.1.3.2 on a GC/FID system (for each GC column, primary and secondary) meeting the initial calibration and continuing calibration technical acceptance criteria.

12.1.3.4.2 The concentration of each of the target analytes in the instrument blank must be less than 0.5 times the CRQL for that analyte.

12.1.3.4.3 The instrument blank must meet all sample analysis technical acceptance criteria in Section 11.3.4 to 11.3.6.

12.1.3.4.4 Surrogate recoveries must fall within the acceptance windows of 70-130%.

12.1.3.5 Corrective Action for Instrument Blanks

12.1.3.5.1 If analytes are detected in the instrument blank at greater than one-half the CRQL, or the surrogate RTs are outside the RT windows, or the surrogate recovery does not meet the acceptance criteria listed in Section 12.1.3.4.4, all data collection must be stopped and corrective action must be taken. Data for samples which were analyzed between the last compliant instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be analyzed before additional data are collected. After an acceptable instrument blank is analyzed, all samples which were considered suspect as defined by the criteria described above must be reinjected during a valid analytical sequence at no additional cost to the Agency and must be reported.

12.1.3.5.2 If the technical acceptance criteria for instrument blank analyses are not met, then the contractor must stop and correct the problem before continuing the analytical sequence. If sample analyses are reported with non-compliant instrument blanks, then the contractor shall receive a commensurate reduction in sample price or zero payment depending upon the impact of the non-compliance on data usability.

12.1.4 Storage Blanks

12.1.4.1 Summary of Storage Blanks

Upon receipt of the first samples in an SDG, two 40.0 ml screw-cap volatile vials with PTFE-faced silicone septa are filled with reagent water and capped so no headspace is present. The vials are stored along with the samples in the SDG under the same storage conditions. The storage blank is analyzed concurrently with the last sample in the SDG. The storage blank indicates whether contamination may have occurred during storage of samples.

12.1.4.2 Frequency of Storage Blanks

A separate storage blank (two 40 ml vials) must be prepared and stored with each SDG. The storage blank must be analyzed concurrently with the last sample in the SDG.

12.1.4.3 Procedure for Storage Blanks

12.1.4.3.1 Pipet a 5 ml aliquot of the storage blank to a separate 10 ml vial, add 10 µl surrogate spiking solution (Section 7.2.4.1) and swirl gently to mix. Transfer a portion of the sample to a 2 ml GC vial and proceed with the GC/FID analysis.

12.1.4.3.2 Analyze the instrument blank according to Section 10 at the frequency listed in Section 12.1.3.2.

12.1.4.3.3 Calculate the concentration of each analyte detected in the storage blank using equation 7. Compare the results to one-half the CRQL values for target compounds in water samples.

12.1.4.4 Technical Acceptance Criteria for Instrument Blanks

12.1.4.4.1 The storage blank must be analyzed on a GC/FID system (for each GC column, primary and secondary) meeting the initial calibration and continuing calibration technical acceptance criteria. The storage blank must be analyzed at the frequency described in Section 12.1.4.2.

12.1.4.4.2 The surrogate recovery must fall within the acceptance window of 70-130%.

12.1.4.4.3 The storage blank must meet all sample analysis technical acceptance criteria in Section 11.3.4 to 11.3.6.

12.1.4.4.4 The concentration of each of the target analytes in the storage blank must be less than 0.5 times the CRQL for that analyte.

12.1.4.5 Corrective Action for Storage Blanks

12.1.4.5.1 If the storage blank does not meet the technical acceptance criteria listed in Sections 12.1.4.4.1 through 12.1.4.4.3, then correct system problems and reanalyze the storage blank. If the storage blank does not meet the technical acceptance criteria in Section 12.1.4.4.4, then reanalyze the storage blank to determine whether the contamination occurred during storage or during the analysis. If, upon reanalysis, the storage blank meets the technical acceptance criteria listed in Section 12.1.4.4, then the problem occurred during the analysis and the reanalyzed storage blank results must be reported. If upon reanalysis, the storage blank did not meet the technical acceptance criteria listed in Section 12.1.4..4.4, then the problem occurred during storage. The laboratory manager or his/her designee must address the problem in the SDG Narrative and discuss the corrective actions implemented to prevent future occurrences. Report storage blank results on a Form I, which must meet all requirements in Exhibit B, and be included with the data package.

12.1.4.5.2 If the technical acceptance criteria for storage blank analyses are not met, then the contractor must stop and correct the problem before continuing the analytical sequence. If sample analyses are reported with a non-compliant storage blank, then the contractor shall receive a commensurate reduction in sample price or zero payment depending upon the impact of the non-compliance on data usability.

12.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the direct aqueous injection methods used for water soluble organics analyses, the Agency has prescribed a mixture of target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method.

12.2.2 Frequency of MS/MSD Analysis

12.2.2.1 A matrix spike and matrix spike duplicate must be prepared/extracted and analyzed for each group of samples of a similar matrix for the following, whichever is more frequent:

- Each SDG (not to exceed 20 field samples), or
- Each matrix within an SDG, or
- Whenever samples are prepared/extracted.

12.2.2.2 As a part of the Agency's QA/QC program, aqueous equipment and/or trip blanks (field QC) may accompany soil/sediment samples and/or water samples that are delivered to a laboratory for analysis. The Contractor shall not perform MS/MSD analysis on any of the designated field QC samples.

12.2.2.3 If the EPA Region designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample volume to perform an MS/MSD, then the Contractor shall contact the RSCC to ascertain an alternate sample to be used for the MS/MSD analysis. The Contractor shall document the affected EPA sample numbers, the Region's instructions, and the date of contact in the SDG Narrative.

12.2.2.4 If there is insufficient sample volume in any of the samples in an SDG to perform an MS/MSD, then the Contractor shall immediately contact the RSCC to report the problem. The Region will either approve that no MS/MSD is required, or require that a reduced sample aliquot be used for the unspiked sample and MS/MSD analysis, or that the unspiked sample is analyzed at full volume and the MS/MSD is analyzed at reduced volume. The RSCC will notify the Contractor of the resolution. The Contractor shall document the decision in the SDG Narrative.

12.2.2.5 The Contractor will not be paid for MS/MSD analysis performed at a greater frequency then required by the contract. If it appears that the Region has requested MS/MSD analysis at a greater frequency then required by the contract, the Contractor shall contact the RSCC to determine which samples should have an MS/MSD performed on them. The RSCC will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative.

12.2.2.6 The Contractor shall not perform MS/MSD analysis on any designated Performance Evaluation samples.

12.2.2.7 If the Contractor has a question regarding the frequency, etc., of the MS/MSD analyses for a particular SDG, contact the RSCC for clarification.

12.2.3 Procedure for Preparing MS/MSD

12.2.3.1 Water Samples

For water samples, pipet two additional 5 ml aliquots of the sample chosen for spiking. Fortify each sample with 10 µl of the matrix spiking solution (Section 7.2.4.2) for a nominal concentration of 400 µg/L. Add 10 µl of surrogate spiking solution (Section 7.2.4.1) to each sample and swirl to mix. Analyze MS/MSDs according to section 10.

12.2.3.2 Soil/Sediment/Solid Samples

For soil/sediment/solid samples weigh out two additional 1.5-2 g aliquots of the sample chosen for spiking into tared 40 ml vials. Record the sample weight to the nearest 0.01 g. Re-tare the vials and to each add 100 µl of matrix spiking solution (Section 7.2.4.2), 100 µl of surrogate spiking solution (Section 7.2.4.1) and fill them with reagent water and cap so there is no headspace. Dry the outside of the vials with an absorbent cloth and re-weigh each vial (to the nearest 0.1 g) to determine the weight of water present, and thus the volume of water to the nearest milliliter.

The expected spike concentration in the MS/MSD will be approximately 500 µg/L for the target compounds and 200 µg/L for the surrogate compound. Extract and analyze matrix spike and matrix spike duplicate according to Section 10.

12.2.4 Calculations for MS/MSD

12.2.4.1 Calculate the concentrations of the matrix spike compounds using equations 7 and 8.

12.2.4.2 Calculate the recovery of each matrix spike compound using the following equation:

EQ. 13

$$Matrix\ Spike\ \%\ Recovery = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spike sample result
SR = Sample result
SA = Spike added

12.2.4.3 Calculate the relative percent difference (RPD) of the recoveries of each compound in the matrix spike and matrix spike duplicate as follows:

EQ. 14

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

Where,

RPD = Relative percent difference
MSR = Matrix spike recovery
MSDR = Matrix spike duplicate recovery

12.2.4.4 The vertical bars in the formula above indicate the absolute value of the difference, hence the RPD is always expressed as a positive value.

12.2.5 Technical Acceptance Criteria for MS/MSD

12.2.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. If the results of the unspiked sample associated with the MS/MSD for all of the target compounds are less than the CRQLs, second column confirmation of the MS/MSDs shall not required and the MS/MSD recoveries shall be reported using the primary column analyses.

12.2.5.2 All MS/MSDs must be prepared and analyzed at the frequency described in Section 12.2.2 using the procedure above and in Section 10 on a GC/FID system meeting the initial calibration (Section 9.2) and continuing calibration (Section 9.3) technical acceptance criteria.

12.2.5.3 All MS/MSDs must have associated method blanks, storage blanks, and instrument blanks meeting their respective blank technical acceptance criterias defined in Section 12.1.

12.2.5.4 The samples must be prepared/extracted and analyzed within the contract required holding times.

12.2.5.5 The retention time for the surrogate must be within the retention time window as established in Section 9.2.4.2 for both GC columns.

12.2.5.5 The percent recovery of each matrix spike compound must be between 60-140 % and the RPD must be ≤30 %. As these limits are only advisory, no further action by the laboratory is required if these limits are not achieved. However, frequent failures to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questioning from the Agency.

12.2.6 Corrective Action for MS/MSD

Any MS/MSD which fails to meet the technical acceptance criteria specified in Section 12.2.5 must be reanalyzed at no additional cost on the Agency. Both sets of data must be reported in accordance with Exhibit B.

12.2.6.1 Corrective actions for failure to meet initial and continuing calibration technical acceptance criteria must be completed before the analysis of any QC samples.

12.2.6.2 Corrective actions for failure to meet the technical acceptance criteria for required blanks must be met before the analysis of any QC samples.

12.2.6.3 If the technical acceptance criteria for the MS/MSD analyses are not met, then the contractor shall determine whether the non-compliance is due to the sample matrix, the sample preparation and/or GC system problems.

12.2.6.4 To determine if the non-compliance is due to sample preparation or GC system problems, check calculations, sample preparation logs, the matrix spiking solution, and the instrument operation. If the

calculations were incorrect, correct the calculations and verify the MS/MSD recoveries. If the sample preparation logs indicate that the incorrect amount of matrix spiking solution was added, then re-prepare/re-extract and reanalyze the MS/MSD after adding the correct amount of matrix spiking solution. If the matrix spiking solution was improperly prepared, concentrated, or degraded, re-prepare the solution and re-prepare/re-extract and reanalyze the MS/MSD. If the instrument malfunctioned, correct the instrument problem and reanalyze the MS/MSD. Re-verify all MS/MSD recoveries. If the instrument malfunction affected the calibrations, recalibrate the instrument before reanalyzing the MS/MSD.

12.2.6.5 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was a matrix effect, take the following corrective action steps:

- Reanalyze the MS/MSD samples.
- If the MS/MSD recoveries meet the technical acceptance criteria in the reanalyzed sample, then the problem was within the Contractor's control. The contractor should make every effort to reanalyze the sample within the contract required holding times. If the reanalysis was performed within holding times, then submit data only from the reanalysis. If the reanalysis was performed outside holding times, then submit both sets of data.
- If the MS/MSD recoveries fail to meet the acceptance criteria in the reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables using the suffixes described in Exhibit B.

12.3 SDG-Specific Performance Evaluation (PE) Samples

12.3.1 Summary of SDG-Specific PE Samples

The Region I Performance Evaluation (PE) program has two functions, (1) to evaluate laboratory operation and protocols over a period of time, and (2) to provide information on the quality of individual data packages.

12.3.2 Frequency of SDG-Specific PE Samples

12.3.2.1 The Region shall submit PE samples with every SDG per parameter, matrix and concentration level (as available). The Region may obtain these SDG-Specific PE samples from either a commercial vendor or from the CLP National Program Office (NPO) which provides PE samples in support of the Superfund program. PE samples provided by the CLP-NPO are referred to as "EPA generated".

12.3.2.2 When the Region submits aqueous trip and/or equipment blanks and/or Performance Evaluation samples (PEs) with soil/sediment/solid field samples, then the Contractor shall not perform an MS/MSD analysis on the aqueous matrix (trip blank, equipment blank, PE sample). When the Region submits an aqueous PE sample with aqueous field samples, then the Contractor shall not choose the PE sample for MS/MSD analysis.

12.3.2.3 If the PE sample is received as an ampulated standard extract, the ampulated PE sample is not considered to be another matrix type.

12.3.3 Procedure for Preparing SDG-Specific PE Samples

12.3.3.1 Instructions for preparation of the PE samples will be included with each submission of PE samples.

12.3.3.2 If PE sample directions do not apply to a PE sample received, then the Contractor must contact the RSCC to ascertain whether or not to analyze the PE sample and to obtain appropriate PE sample directions.

12.3.4 Calculations for SDG-Specific PE Samples

For EPA-generated and commercially prepared PE samples that are submitted with each SDG, the Contractor must correctly identify and quantitate all TCL compounds using the criteria presented in Section 11.0 - Data Analysis and Calculations.

12.3.5 Technical Acceptance Criteria for SDG-Specific PE Samples

12.3.5.1 All SDG-Specific PE samples must be analyzed under the same GC/FID conditions established in Section 9.0 and must meet the same technical acceptance criteria established for sample analysis defined in Section 11.3.

12.3.5.2 EPA-generated PE samples included with the SDG will be evaluated by the Region using a CLP NPO computer program called PeacTOOLs. PeacTOOLs rates the PE sample results based on statistically generated confidence intervals.

12.3.5.3 The results of commercially prepared PE samples will be evaluated using the vendors' statistically generated confidence intervals.

12.3.5.4 Contractor results for the SDG-Specific PE samples will be evaluated using the most recent Region I data validation criteria for PE samples.

12.3.5.5 At a minimum, the PE results will be evaluated for compound identification, quantitation, and sample contamination. Confidence intervals for the quantitation of target compounds are based on reported values using population statistics. The Agency may adjust the criteria on any given PE sample to compensate for unanticipated difficulties with a particular sample. Some of the compounds spiked into the PE sample may not be those specifically listed in Exhibit C, Water Soluble Organics - NPD. Thus, if appropriate, the Contractor must use the guidelines described in Section 11.1.2 to confirm identification of possible target compounds.

12.3.6 Corrective Action for SDG-Specific PE Samples

12.3.6.1 The corrective actions for PE sample results which do not meet the technical acceptance criteria defined in Section 12.3.5.1 are the same corrective actions outlined for sample analysis in Section 11.4.

12.3.6.2 If an SDG-Specific PE sample evaluated by Region I, as described in Sections 12.3.5.2 through 12.3.5.5, indicates unacceptable laboratory performance, then the Contractor may be required to reanalyze all samples, standards, blanks and QC samples associated with the unacceptable PE sample result (if sufficient sample volume remains) and/or analyze a new PE sample at no additional cost to the Agency. Unacceptable laboratory performance includes either a TCL false positive result, false negative result, and/or compound misquantitation (reported result exceeds ± 3 sigma of the spiked compound concentration).

12.3.6.3 Sample results reported with unacceptable SDG-Specific PE results may be subject to a commensurate reduction in sample price or zero payment due to data rejection, depending upon the impact of the non-compliance on data usability.

13.0 METHOD PERFORMANCE

Not Applicable

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions.

16.0 REFERENCES

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16.3 Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters: Category 11 - Purgeables and Category 12 Acrolein, Acrylonitrile, and Dichlorodifluoromethane, Report for EPA Contract 68-03-2635 (in preparation).

16.4 Standard Test Method for Volatile Alcohols in Water by Direct Aqueous-Injection Gas Chromatography, Method D 3695, Annual Book of ASTM Standards, Volume 11.02, Water.

16.5 "Test Methods for Evaluating Solid Waste Physical/Chemical Methods", USEPA, SW 846/8015A, third edition and updates, July, 1992.

16.6 Volatile Organic Compounds Specific to the Pharmaceutical Manufacturing Industry by GC/FID, Method 1671 in Analytical Methods for the Determination of Pollutants in Pharmaceutical Manufacturing Industry Wastewater, EPA-821-B-94-001, February, 1995.